

REGENERATION OF A PHOSPHORUS-CONTAINING SORBENT

Cross-reference to Related Applications

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[001] This application is a continuation-in-part application of U.S. Patent Application No. 09/566,461, filed on May 8, 2000. The application also is related to U.S. Patent No. 6,492,568, issued December 10, 2002.

Field of the Application

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[002] The application relates to a process for regenerating non-combustible sorbents comprising one or more combustible impurities comprising phosphorus.

Background

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[003] Depending upon the method of their production, olefin feedstocks may comprise a variety of impurities. Impurities found in olefins that are produced by oligomerization of ethylene units may include phosphorus-containing impurities, including but not necessarily limited to organophosphines and organophosphine oxides. These phosphorus-containing impurities are largely removed from many olefin streams during the process of distillation to separate various "cuts" of olefins. Unfortunately, the organophosphines and organophosphine oxides found in C₁₄-C₁₈ streams tend to codistill with the C₁₄-C₁₈ in the product, making it difficult, if not impossible to remove these phosphine impurities by simple distillation.

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[004] C₆-C₃₆ olefins have utility in the fields of paper and pulp processing, drilling fluids, and machine or metal working oils. Alcohols of such olefins have commercial importance in a variety of applications, including detergents, soaps, surfactants, and freeze point depressants in lubricating oils. These alcohols are produced by a number of commercial processes, such as by oxo or hydroformylation of long chain olefins. In many of these applications, the olefin feedstocks are treated using acid catalysts.

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[005] Unfortunately, phosphorus-containing impurities in these olefin feedstocks can negatively affect acid catalysts. The phosphorus-containing moieties that are basic in nature will neutralize the active acid sites of the catalyst, which lowers catalyst activity and performance. The organophosphine moieties may even cause the
5 olefins to oligomerize into undesirable forms.

[006] Methods are needed to reduce the phosphorus-content of olefin feedstocks.

Summary

[007] The application provides a process for regenerating non-combustible sorbents comprising one or more combustible impurities comprising phosphorus. The
10 process comprises providing one or more spent non-combustible sorbents comprising a content of said one or more combustible impurities comprising phosphorus, and exposing the one or more non-combustible sorbents to regeneration conditions effective to remove the combustible impurities comprising phosphorus and to produce a regenerated sorbent effective to sorb 80 wt.% or more of the content of one or more
15 combustible impurities comprising phosphorus.

Detailed Description

[008] The present application provides a process for regenerating substantially any non-combustible sorbent comprising combustible impurities comprising phosphorus. In a preferred embodiment, the process is used to regenerate non-combustible sorbents
20 used to reduce the content of phosphorus-containing impurities in olefin streams, more preferably linear olefin streams made by oligomerizing ethylene.

[009] Some of the known processes for oligomerizing ethylene use organo-phosphorus compounds that result in combustible impurities comprising phosphorus, such as organophosphines and organophosphine oxides, as a contaminant in the
25 resulting olefin stream. A preferred commercially available olefin feed for the

treatment using the non-combustible sorbents of the present invention is the product marketed in the United States by Shell Chemical Company under the trademark NEODENE[®]. In a preferred embodiment, the olefin feedstock is treated before exposure to an acid catalyst, or before exposure to other conditions which would be adversely affected by the basic nature of certain combustible impurities comprising phosphorus.

[0010] A preferred process for treating the olefins in order to create the spent non-combustible sorbents described herein is described in detail in U.S. Patent No. 6,492,568, incorporated herein by reference.

10 **Acidic Zeolites and Aluminas as Sorbents**

[0011] The non-combustible sorbent regenerated using the process described herein may be substantially any non-combustible sorbent capable of sorbing combustible impurities comprising phosphorus, preferably combustible basic impurities comprising phosphorus. Most preferably, the non-combustible sorbents are effective to absorb organophosphines and organophosphine oxides from an olefin stream. Suitable non-combustible sorbents include, but are not necessarily limited to acidic zeolite, acidic alumina, and/or neutral alumina. Suitable aluminas are commercially available in a variety of morphologies, described below, and also may be extruded as a paste using an acidic or neutral alumina powder. An example of a suitable commercially available neutral alumina is SELECTO SCIENTIFIC[®] Neutral alumina. Where an extrudate is made, the "paste" suitably is extruded or otherwise molded into a variety of shapes, including but not necessarily limited to a multilobed cylindrical form. The resulting material preferably is dried at temperatures of at least about 100 °C. and calcined at about 500 °C. or more in the presence of flowing air in a muffle furnace or purged high temperature air drier or rotary calciner.

Metal or Metal Oxide on a Support

[0012] In another embodiment, the non-combustible sorbents comprise a suitable metal or metal oxide on a support. In this embodiment, preferred metals are transition metals, including but not necessarily limited to those selected from Groups 3-12 of the Periodic Table of the Elements. When the Periodic Table of the Elements is referred to herein, the source of the Periodic Table is: F. Cotton et al. Advanced Inorganic Chemistry (5th Ed. 1988). Suitable metals include, but are not necessarily limited to Sc, V, Cr, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mn, Ag and combinations thereof. Preferred metals are Fe, Co, Ni, Mn, Ag and Cu. More preferred metals are silver or copper, preferably in the form of oxides. In this embodiment, the sorbent suitably comprises from about 0.1 wt. % to about 50 wt. % of the metal oxide of the foregoing metals, preferably copper. Preferably, the sorbent comprises from about 1 wt. % to about 20 wt. %, more preferably from about 5 wt. % to about 15 wt. %, and most preferably from about 8 wt. % to about 10 wt. % of the metal oxide.

[0013] Suitable supports are non-combustible supports that do not combust under regeneration conditions (i.e., while contacting the support material with an oxygen containing gas at elevated temperatures). Suitable non-combustible support materials include, but are not necessarily limited to acidic and neutral non-combustible support materials. Preferred acidic non-combustible support materials include, but are not necessarily limited to acidic aluminas, silica, molecular sieves, such as zeolites, aluminosilicate clays, and the like. Preferred non-combustible neutral support materials include, but are not necessarily limited to neutral aluminas. A most preferred non-combustible support material is an acidic non-combustible support material including, but not necessarily limited to acidic aluminas and acidic zeolites.

Commercially available acidic aluminas include, but are not necessarily limited to

neutral alumina, available from Selecto Scientific Co. Also suitable are the modified aluminas, such as SELEXSORB CDO 200, SELEXSORB CDX, AND SELEXSORB CD. These aluminas are modified to improve the sorption of polar organics, and are commercially available from Alcoa Industrial Chemicals.

- 5 **[0014]** Suitable commercially available sorbents comprising copper on alumina include, but are not necessarily limited to SELEXSORB ASTM, commercially available from Alcoa Industrial Chemicals, and KL5715, commercially available from CRI, Inc.

- 10 **[0015]** Whether the sorbent is acidic zeolite or alumina, alone, or a supported metal or metal oxide, the surface area of the sorbent is not critical. A preferred surface area is about 10 m²/g or more in order to provide sufficient contact between the sorbent and the olefin stream. In a preferred embodiment, the sorbent has a surface area of from about 100 m²/g to about 900 m²/g. It is preferred for the sorbent particles to be as small as possible; however, if the size of the particles is too small, the pressure
- 15 drop through the bed becomes too large. Very small particles also are difficult to retain in the sorbent bed. The particles may have substantially any form, including but not necessarily limited to spherical form, tablet form, cylindrical form, multilobed cylindrical forms, and their corresponding hollow counterparts. In a preferred embodiment, the particles have a diameter of from about 50 mesh to about 6 mm,
- 20 preferably about 0.8 mm (1/32 inch) to about 1.6 mm (1/16 inch), most preferably about 0.8 mm. The length of the particles is not critical, with suitable lengths including, but not necessarily limited to less than about 10 mm, preferably from about 3 mm to about 5 mm.

Regeneration Conditions

[0016] The sorbent is regenerated by first rinsing the sorbent with an amount of solvent necessary to displace the olefin. Suitable solvents include, but are not necessarily limited to hydrocarbons such as cyclohexane, butanes, pentanes, hexanes, 5 heptanes, octanes, cyclopentane, butenes, and octenes. A preferred solvent is cyclohexane. In another embodiment, the olefin may be displaced by passing a gas through the sorbent bed to strip off the olefin. Suitable gases include, but are not necessarily limited to nitrogen, argon, and mixtures thereof. Once any strippable combustible impurities comprising phosphorus are stripped from the sorbent, the 10 sorbent is allowed to dry out.

[0017] Once dry, the sorbent is exposed to regeneration conditions. The regeneration conditions comprise an oxygen-containing atmosphere and a temperature sufficiently high to combust or remove the combustible impurities comprising phosphorus but sufficiently low to avoid damaging the sorbent. Suitable temperatures 15 are from about 200 °C. to about 700 °C., preferably from about 450 °C. to about 600 °C. The regeneration conditions are effective to combust at least about 80 wt.% or more, preferably about 90 wt.% or more, more preferably about 95 wt.% or more, most preferably substantially all of the combustible impurities comprising phosphorus present on the sorbent. The period of time for which exposure to the elevated 20 temperature is required will vary, but generally is from about 0.5 hour to about 200 hours, preferably about 100 hours. For purposes of the present application, the regeneration conditions do not damage the sorbent if they produce a regenerated sorbent that is effective to sorb 80 wt.% or more, preferably 90 wt.% or more, more preferably 95 wt.% or more, most preferably substantially all combustible impurities

comprising phosphorus present in a stream, such as an olefin stream, subsequently treated with the regenerated sorbent.

[0018] Suitable oxygen containing atmospheres include, but are not necessarily limited to air, oxygen gas, and a combination of oxygen gas with nitrogen gas.

5 Suitable gases comprise about 0.001% or more oxygen, more suitably from about 0.5 to about 21% oxygen (the typical content of air). A preferred gas is a commercially available combination comprising from about 0.5 to about 1% oxygen, with the remainder being nitrogen. Higher oxygen contents may be used after the majority of the combustible material has been removed. Higher oxygen contents facilitate the
10 removal of combustible materials.

[0019] The process may be conducted under a wide range of pressures. Suitable pressures are from about 0.01 MPa (about 0.1 atm) to about 50 MPa (about 500 atm), preferably from about 0.1 MPa (about 1 atm) to about 10 MPa (about 100 atm). A suitable flow rate for the oxygen containing atmosphere is from about 0.001 to about
15 50 liters/hour per gram catalyst. Where the oxygen containing atmosphere is air, a preferred flow rate is from about 0.1 to about 5 liters/hour per gram catalyst. The regeneration process may be conducted at an elevated pressure, as described in U.S. Patent No. 5,648,585, incorporated herein by reference. Such elevated pressure conditions include those where the oxygen partial pressure is greater than atmospheric
20 air.

[0020] After exposure to the elevated temperature(s) for a period of time of from about 0.5 hour to about 200 hours, preferably about 100 hours, the bed is cooled to at least about 100 °C., and preferably to about 25 °C., or ambient temperature, in order to avoid overheating upon rewetting of the sorbent. The cooled bed is purged with
25 nitrogen or air before reuse in the process. Nine regeneration cycles under these

conditions have been shown to produce no loss in sorbent capacity. Some slight loss in sorbent capacity was seen beginning after 10 regeneration cycles.

[0021] The invention will be better understood with reference to the following examples, which are illustrative only and not intended to limit the invention to any particular embodiment.

EXAMPLE I

[0022] One gram of SELEXSORB ASTM (crushed to 20 x 40 mesh) was equilibrated with 550 grams of NEODENE[®] 16 containing about 20 ppm phosphorus. The sorbent and the olefin were then separated and the olefin was analyzed to determine the uptake of phosphorus by the sorbent. Following this, the sorbent was regenerated by the following procedure:

- a. The sorbent was rinsed with from about 75 to about 100 ml. cyclohexane per gram of sorbent to displace the olefin;
- b. The rinsed sorbent was heated under air flow at 125°C. for 6 minutes;
- 15 c. The temperature was increased at 3° C./min to 200° C. and held for 2 hours;
- d. The temperature was increased at 2° C./min to 500° C. and held for 2 hours;
- and
- e. The regenerated sorbent was cooled in air to ambient temperature.

[0023] The regenerated sorbent was contacted with a fresh batch of NEODENE[®] 16 at the same weight ratio of 550 gm NEODENE[®] 16 to 1 gm sorbent. This procedure was repeated for a total of 14 sorption cycles and 13 regeneration cycles. The capacity of the sorbent for phosphorus after each cycle was calculated and compared to the capacity data for the virgin sorbent. The results are given in the following Table:

| Equilibrium P (ppm) | Virgin Sorbent | Regen 1X | Regen 2X | Regen 3X | Regen 6X | Regen 9X | Regen 12X | Regen 13X |
|------------------------|-------------------|-------------|-------------|-------------|-------------|-------------|--------------|--------------|
| 0 | 0 | | | | | | | |
| 0.5 | 0.16 | | | | | | | |
| 2.2 | 0.36 | | | | | | | |
| 2.5 | 0.26 | | | | | | | |
| 2.6 | 0.43 | | | | | | | |
| 4.9 | 0.52 | | | | | | | |
| 7.5 | | 0.55 | | | | | | |
| 7.7 | | | | 0.51 | | | | |
| 7.8 | 0.54 | | | | | | | |
| 8.4 | 0.47 | | | | | | | |
| 8.5 | | | 0.46 | | | | | |
| 9.7 | 0.56 | | | | | | | |
| 10.4 | | | | | 0.51 | | | |
| 12.6 | | | | | | | | 0.36 |
| 13.6 | | | | | | 0.6 | | |
| 14.2 | | | | | | | 0.3 | |

After 9 regenerations (10 sorption cycles) the capacity of the sorbent was still comparable to that of the virgin material. However, a decline in capacity was observed after the tenth regeneration.

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EXAMPLE II

[007] NEODENE[®] 16 (containing 20 ppm phosphorus) was added to a jar containing zeolite X with 35% silver by weight (commercially available as silver-exchanged zeolite from Aldrich Chemical Company, Inc.). The zeolite particles were sized to 20 x 40 mesh and shaken intermittently by a flat bed shaker over a period of 15 hours at 23°C to achieve equilibration. The NEODENE[®] 16 to silver containing X-zeolite weight ratio was 100:1. A similar experiment was conducted with a NEODENE[®] 16 to silver containing X-zeolite weight ratio of 400:1 After equilibration, the NEODENE[®] 16 was separated from the sorbent and analyzed for phosphorus using inductively coupled plasma. The results are given in the following Table:

| Sorbent | Equilibrium P (ppm) | P loading (g/100 g sorbent) | NEODENE® 16 to Sorbent Weight Ratio |
|---------------------------|---------------------|-----------------------------|-------------------------------------|
| Ag Zeolite X (35% wt. Ag) | <2 | >0.18 | 100:1 |
| Ag Zeolite X (35% wt. Ag) | 6.3 | 0.39 | 400:1 |

[007] Following this, the sorbent (Ag Zeolite X) was regenerated by the following procedure:

- 5 a. The sorbent was rinsed with from about 75 to about 100 ml. cyclohexane per gram of sorbent to displace the olefin;
- b. The rinsed sorbent was heated under 1% oxygen in balanced nitrogen flow at 125°C. for 6 minutes;
- c. The temperature was increased at 3° C./min to 200° C. and held for 2 hours;
- 10 d. The temperature was increased at 2° C./min to 500° C. and held for 2 hours, and then the 1% oxygen in balanced nitrogen was replaced by flowing air and the temperature was held at 500° C for an additional 2 hours; and
- e. The regenerated sorbent was cooled in air to ambient temperature.

[008] After regeneration, the Ag Zeolite X (35% wt.) samples were placed

15 separately into jars. NEODENE® 16 (containing 20 ppm phosphorus) was added to the jars containing zeolite X with 35% silver by weight. NEODENE® 16 to silver containing X-zeolite weight ratios of 100:1 and 400:1 were again used with the corresponding regenerated samples. The zeolite particles (20 x 40 mesh) were shaken intermittently by a flat bed shaker over a period of 15 hours at 23°C to achieve

20 equilibration. After equilibration, the NEODENE® 16 was separated from the sorbent

samples and analyzed for phosphorus using inductively coupled plasma. The results are given in the following Table:

| Sorbent | Equilibrium P (ppm) | P loading (g/100 g sorbent) | NEODENE® 16 to Sorbent Weight Ratio |
|---------------------------------------|---------------------|-----------------------------|-------------------------------------|
| Regenerated Ag Zeolite X (35% wt. Ag) | <2 | — | 100:1 |
| Regenerated Ag Zeolite X (35% wt. Ag) | 5.9 | 0.39 | 400:1 |

- 5 The results show that regenerated silver containing zeolite sorbent achieves a level of phosphorus removal similar to that of fresh sorbent by the procedure used.

EXAMPLE III

- 10 [007] NEODENE® 16 (containing 20 ppm phosphorus) was added to a jar containing SELECTO SCIENTIFIC® Neutral alumina sorbent. The alumina sorbent particles were sized to 20 x 40 mesh and shaken intermittently by a flat bed shaker over a period of 15 hours at 23°C to achieve equilibration. After equilibration, the NEODENE® 16 was then separated from the sorbent.
- 15 [008] Following this, the sorbent was regenerated by the following procedure:
- a. The sorbent was rinsed with from about 75 to about 100 ml. cyclohexane per gram of sorbent to displace the olefin;
 - b. The rinsed sorbent was heated under 1% oxygen in balanced nitrogen flow at 125°C. for 6 minutes;
 - 20 c. The temperature was increased at 3° C./min to 200° C. and held for 2 hours;
 - d. The temperature was increased at 2° C./min to 500° C. and held for 2 hours,

and then the 1% oxygen in balanced nitrogen was replaced by flowing air and the temperature was held at 500° C for an additional 2 hours; and

e. The regenerated sorbent was cooled in air to ambient temperature.

[009] After regeneration, the sample was placed in a jar and NEODENE® 16

5 (containing 22 ppm phosphorus) was added to the jar. The NEODENE® 16 to sorbent weight ratio used was 100:1. The jar was shaken intermittently by a flat bed shaker over a period of 15 hours at 23°C to achieve equilibration. After equilibration, the NEODENE® 16 was separated from the sorbent and analyzed for phosphorus using inductively coupled plasma. The results are given in the following Table:

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| Sorbent | Equilibrium P (ppm) | P loading (g/100 g sorbent) |
|---|---------------------|-----------------------------|
| SELECTO SCIENTIFIC® Neutral alumina Fresh | 2.9 | 0.14 |
| SELECTO SCIENTIFIC® Neutral alumina Regenerated | 2.9 | 0.14 |

The results show that regenerated alumina sorbent can achieve a level of phosphorus removal similar to that of fresh sorbent by the procedure used.

[007] Persons of ordinary skill in the art will recognize that many modifications

15 may be made to the present invention without departing from the spirit and scope of the present invention. The embodiment described herein is meant to be illustrative only and should not be taken as limiting the invention, which is defined in the following claims.